Study of PM_{10} and $PM_{2.5}$ levels in three European cities: Analysis of intra and inter urban variations

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HIGHLIGHTS

- Sources and factors affecting PM are investigated in Athens, London and Madrid.
- EU PM limit values are frequently breached forming a potential public health hazard.
- Contribution of secondary/natural PM in summertime is higher in Athens and Madrid.
- Contribution of non-combustion sources varies among cities, sites and seasons.
- Non-combustion fraction of both PM metrics is higher during summer at all sites.

ABSTRACT

In the present paper, 1-year PM_{10} and $PM_{2.5}$ data from roadside and urban background monitoring stations in Athens (Greece), Madrid (Spain) and London (UK) are analysed in relation to other air pollutants (NO, NO_2, NO_x, CO, O_3 and SO_2) and several meteorological parameters (wind velocity, temperature, relative humidity, precipitation, solar radiation and atmospheric pressure), in order to investigate the sources and factors affecting particulate pollution in large European cities. Principal component and regression analyses are therefore used to quantify the contribution of both combustion and non-combustion sources to the PM_{10} and $PM_{2.5}$ levels observed. The analysis reveals that the EU legislated PM_{10} and $PM_{2.5}$ limit values are frequently breached, forming a potential public health hazard in the areas studied. The seasonal variability patterns of particulates varies among cities and sites, with Athens and Madrid presenting higher PM_{10} concentrations during the warm period and suggesting the larger relative contribution of secondary and natural particles during hot and dry days. It is estimated that the contribution of non-combustion sources varies substantially among cities, sites and seasons and ranges between 38–67% and 40–62% in London, 26–50% and 20–62% in Athens, and 31–58% and 33–68% in Madrid, for both PM_{10} and $PM_{2.5}$. Higher contributions from non-combustion sources are found at urban background sites in all three cities, whereas in the traffic sites the seasonal differences are smaller. In addition, the non-combustion fraction of both particle metrics is higher during the warm season at all sites. On the whole, the analysis provides evidence of the substantial impact of non-combustion sources on local air quality in all three cities. While vehicular exhaust emissions carry a large part of the risk posed on human health by particle exposure, it is most likely that mitigation measures designed for their reduction will have a major effect only at traffic sites and additional measures will be necessary for the control of background levels. However, efforts in mitigation strategies should always focus on optimal health effects.

Keywords:
Particulate matter
Air quality
Traffic emissions
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Seasonal variability
Non-combustion sources

1. Introduction

Over the last two decades, several time-series and cohort epidemiological studies have been conducted mainly in the US and Europe to investigate the health significance of ambient particulate

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matter (Dockery and Pope, 1994; Boezen et al., 1999; Samet et al., 2000; Kassomenos et al., 2008) and established the association between human exposure and the risk of increased mortality and morbidity. However, uncertainty remains as to the exact physical properties and chemical components (Sillanpää et al., 2006; Rodríguez et al., 2007; Puustinen et al., 2007) which are responsible for the adverse health-effects, with many studies implicating that exposure to fine and ultrafine particles poses the greatest risk (Janssen et al., 2011; Rückerl et al., 2011; Raaschou-Nielsen et al., 2013). Additionally, the REVIHAAP study confirmed the causal relationship of exposure to $PM_{2.5}$ and adverse health effects (WHO, 2013). The highest PM_{10} and $PM_{2.5}$ concentrations in the European cities occur at the roadside but urban background stations have also recorded relatively high PM_{10} and $PM_{2.5}$ values (Vardoulakis et al., 2011), raising concerns about the exposure of a large proportion of the European urban population to particulate pollution (Vardoulakis and Kassomenos, 2008).

Based on the mounting epidemiological evidence, the EU has legislated limits and guidelines on controlling the levels of both PM_{10} and $PM_{2.5}$ in ambient air and has promulgated two limit values for PM_{10} and a health-based target value for $PM_{2.5}$ (Council Directive 2008/50/EC^{-1}). Specifically, a 24 h mean concentration of 50 μg m^{-3} not to be exceeded more than 35 times per calendar year and an annual mean concentration of 40 μg m^{-3} have been imposed for PM_{10}, while an annual limit value of 25 μg m^{-3} has been set for $PM_{2.5}$ (to be met by 1/1/2015).

In recent years, high levels of PM_{10} and $PM_{2.5}$ have been observed in several European cities, where increased PM_{10} and $PM_{2.5}$ concentrations frequently persist over periods of several days, resulting in exceedances of the relevant EU limit/target values and having severe implications for population exposure. Additionally, recent findings highlight the existence of significant spatial variability in PM levels, both at a regional level and within large urban agglomerations (Hazenkamp-von Arx et al., 2004; Eeftens et al., 2012) and thus the issue of spatial scale is of particular importance for the characterization of particle pollution. At a large geographical scale the variability is driven by differences in emission profiles and intensities, climatic characteristics and long range transport processes. On the other hand, within the urban–suburban setting, PM level contrasts are mainly determined by traffic conditions, local sources and topographic characteristics, leading to large intra-urban variations, with severe implications for the characterization of population exposure. As an example, mobile monitoring showed a large spatial variability, especially for ultrafine particles and black carbon, the combustion-related part of PM (Van Poppel et al., 2013). Thus, the consideration of both the between-area and within-area variability appears rather meaningful. Several multi-country studies across the EU have analysed air quality and meteorological data series to identify the factors influencing particulate pollution levels in various urban settings. For instance, Hoek et al. (1997) analysed PM_{10} concentrations at 28 sites in 10 European countries and found that the differences across countries appear to be considerably larger than the differences among urban and rural locations within countries, with median concentrations ranging between 11 μg m^{-3} (at rural Scandinavian sites) and 92 μg m^{-3} (in Athens, Greece). Houthuijs et al. (2001) analysed PM_{10} and $PM_{2.5}$ concentrations at 25 sites in six Central and Eastern European countries and found a two- to three-fold concentration range among study areas. Additionally, the variation in PM_{10} and $PM_{2.5}$ concentrations among study areas was about 4 times greater than the spatial variation within study areas. Querol et al. (2004b) investigated the origin of PM_{10} in seven European regions using speciated PM_{10} and $PM_{2.5}$ measurements from a range of regional, urban background and kerbside monitoring stations. They concluded that the $PM_{2.5}/PM_{10}$ ratio was highly dependent on the type of site and varied widely among different EU regions. Kukkonen et al. (2005) carried out an analysis of selected episodes in four European cities (Oslo, Helsinki, London and Milan) using available datasets of PM_{10} and meteorological data and concluded that the vast majority of episodes were mainly related to prevalence of specific meteorological conditions (high atmospheric pressure systems and temperature inversions). Vardoulakis and Kassomenos (2008) used 3-year meteorological and pollutant data from traffic and suburban background locations in Athens and Birmingham and found that in Birmingham high PM_{10} concentrations were generally associated with cold weather, anti-cyclonic conditions and easterly winds, providing clear evidence of long-range transport (LRT) of particles from continental Europe, whereas in Athens strong local emissions sources in combination with stagnating or re-circulating air masses gave rise to a larger number of exceedances per year.

While the above-mentioned studies are only a partial list, a more detailed literature review would reveal that large scale studies in Europe most often rely on purpose-designed measurement networks and less on already installed automated monitoring stations. Although the former approach has certain advantages (harmonization of measurement methods, optimal site selection), it comes at a significant cost. In this study we explore the possibility of using only publicly available, fixed-site, pollutant and meteorological data in order to characterize the spatial and seasonal variability of PM levels and to identify their main sources. Specifically, the objective of this work is the examination of PM levels in three major European cities (Athens-Greece, London-UK and Madrid-Spain) with different climatic, topographic and emission-related characteristics. The analysis presented focuses on site-type (traffic-urban background) and seasonal contrasts of PM_{10} and $PM_{2.5}$ and their controlling factors, and also attempts an estimation of combustion and non-combustion contributions to PM levels. The statistical treatment applied to the time-series provides an initial-stage option for delving in the sources and processes affecting particle levels, using only routinely monitored pollutant and meteorological data.

2. Data and methodology

2.1. Data sources

One-year PM_{10}, $PM_{2.5}$, NO, NO_2, NO_x, SO_2, O_3 and CO hourly values from an urban background and a traffic oriented monitoring site were analysed along with local meteorological parameters (wind speed, temperature, relative humidity, precipitation, atmospheric pressure, solar radiation) at the three cities. The study year was 2005 for London and Madrid, while 2007 was selected for Athens, due to the lack of $PM_{2.5}$ time-series with adequate data coverage for a pair of traffic-background sites, during the previous two years. The year 2007 for Athens was considered comparable to 2005 which was selected for the other 2 cities, as a highly significant inter-annual trend was not observed. Specifically, PM_{10} levels measured at 4 sites in the area remained fairly stable (mean annual differences less than 3 μg m^{-3}, all not significant at 0.99 level and only one significant at 0.95 level) while $PM_{2.5}$ at API differed by less than 2 μg m^{-3} (also not significant at the 0.95 level). Similar results were obtained for NO_x trends at the two test sites. Data capture in the yearlong PM datasets was over 90% for London and Madrid and 75–85% for Athens. Missing values for the Athens sites were found to be uniformly distributed between the cold and the warm period and weekends–weekdays. Hence, the relatively lower data coverage is not expected to substantially affect the results. It is also noted that the data were used as ratified and reported to the European Union by monitoring authorities. Specifically, for London

PM_{10} a gravimetric equivalence factor of 1.3 is used, while a correction factor of 1.1 is used for TEOM data in Madrid. No correction is made in Athens.

The selected monitoring locations were: (a) Agia Paraskevi (AAP) and Piraeus (API) in Athens, (b) Bloomsbury (LBL) and Marylebone Road (LMR) in London and (c) Casa de Campos (MCC) and Paseo de Recoletos (MPR) in Madrid. API, LMR and MPR are situated in the city-centres and experience heavy traffic conditions, while AAP, LBL and MCC are urban background sites.

Specifically, API is located in the center of Piraeus, at the south-western part of the greater area of Athens. Measurements were conducted at a kerbside station which experiences heavy traffic and is also in close vicinity to the port of Piraeus. The distance of API to the road is 5 m (kerbside site), while the distance to the nearest major road is approximately 50 m. The combined traffic load within a 50 m radius for API is estimated (traffic sensors and visual counts) at 35,000 vehicles per day. Apart from traffic and marine emissions, this site is also influenced by the commercial/industrial activities related to the operation of the port. On the other hand, AAP is an urban background site, located NE of the city-center, at the foothills of mount Hymettus which forms a natural boundary for the Athens basin. This location is not directly influenced by traffic emissions, whereas intra-urban particle transport and secondary particle formation are considered to be the main processes affecting particle levels in the area (Grivas et al., 2008a).

LMR is located on London Marylebone Road, approximately 1 m away from the extremely busy A50 road, where traffic flows of over 80,000 vehicles per day pass the site on 6 lanes. The road is very frequently congested, while the surrounding area forms a street canyon and comprises of educational buildings, tourist attractions, shops and housing. On the other hand, LBL is located within the north-east corner of a central London garden, surrounded by a busy 2 lane one-way road system, which is subject to frequent congestion. The nearest road lies at a distance of approximately 25 m from the station and the area in the vicinity of the manifold is surrounded by small buildings.

MPR is a traffic station located in central Madrid 10 m away from the wide boulevard of Paseo de Recoletos, leading from Plaza de Cibeles to Plaza de Colón. The area experiences heavy loads of traffic and is also influenced by urban commercial activities. Specifically, the mean daily traffic load, within a 50 m radius around the sites (2 segments of the Paseo de Recoletos Boulevard) is estimated at 70,000 vehicles per day (2008). Traffic on the nearest segment to the station is approximately 30,000 vehicles per day. MCC is installed in the Casa de Campo garden park which covers an area of approximately 1770 ha and is located 4 Km to the west of the city centre of Madrid. More information about the vehicular fleet makeup at the three areas is provided as Supplementary material (Table S1).

The air quality monitoring stations in London and Madrid are equipped with Tapered Element Oscillating Microbalance (TEOM) PM_{10} and $PM_{2.5}$ monitors (precision: 1 μg m^{-3} (24-h)–2 μg m^{-3} (1-h)), whereas Beta Attenuation (BA) PM_{10} and $PM_{2.5}$ monitors (precision: 2 μg m^{-3} (24-h), LOD: 0.5 μg m^{-3} (24-h)–3 μg m^{-3} (1-h)) are used in the air quality monitoring network of Athens (ESM-Andersen, FH, 62 I-R). Results on the agreement/equivalence of continuous monitors to measurements from gravimetric samplers which comply with the reference methods (EN12341:1999, EN:14907:2005) can be found in Green and Fuller (2006) and Grivas et al. (2004) for traffic sites in London and Athens, respectively. Additionally, it is emphasized that although TEOM might underestimate PM concentrations due to losses of semi volatiles (Kulkarni et al., 2011), the Beta monitors used in Athens use pre-heated inlets (50 °C) as well, and therefore suffer from the same artifact. This has been displayed specifically for Athens (Grivas et al., 2004) and elsewhere (Gehrig et al., 2005). Based on reported results (Hauck et al., 2004; Zhu et al., 2007), the difference in long-term average concentrations between Beta and TEOM monitors (simultaneously operated) can be as low as 1.4% and in the majority of cases lower than 5%. However, the exact degree of agreement between methods is considered site specific. It is also noted that there is seasonal effect on the accuracy of both TEOM and Beta methods, introduced by the seasonal variability in ambient concentrations of semi-volatile compounds which are lost during pre-heating of the sampled air stream (Schwab et al., 2006).

Table 1
Seasonal PM_{10}, $PM_{2.5}$ means (in μg m^{-3}), and $PM_{2.5}/PM_{10}$ ratios together with the number of days with 24 h mean $PM_{10} > 50$ μg m^{-3}.

Site	City/type	PM_{10} cold	PM_{10} warm	$PM_{2.5}$ cold	$PM_{2.5}$ warm
AAP	Athens/background	22.69 (1)	32.55 (14)	14.66	22.73
API	Athens/traffic	44.13 (29)	51.22 (56)	32.47	38.48
LBL	London/background	26.56 (4)	26.53 (1)	12.95	12.59
LMR	London/traffic	43.23 (58)	43.87 (64)	19.05	19.40
MCC	Madrid/background	29.06 (25)	34.50 (35)	14.30	13.49
MPR	Madrid/traffic	37.46 (47)	38.87 (46)	24.14	20.63

Standard infrared, chemiluminescence, ultraviolet and fluorescence gas analysers are used to monitor CO, NO–NO_2–NO_x, O_3 and SO_2 respectively at all cities. It is noted that although a BC network is established in London, no continuous data were available at the time of comparison. Therefore, BC measurements were not used. The meteorological data used in the study were collected at Heathrow airport in London and in Casa de Campos in Madrid. In Athens, data from the nearest meteorological stations of Psytaleia and Zografos (METEONET network, http://hoa.ntua.gr) were used for the API and AAP sites respectively.

2.2. Methods

All monitoring data were subdivided in two periods, namely the 'cold' (16 October–15 April) and the 'warm' period (16 April–15 October), in order to disassociate the seasonal factors influencing particulate levels (Argyriou et al., 2004; Vardoulakis and Kassomenos, 2008). The hourly data (both pollutant concentrations and meteorological parameters) were averaged over 24-h periods when at least 75% of hourly data were available for each day, while missing values were excluded from the analysis.

Initially, Pearson correlation analysis was carried out pairing particulates PM_{10} and $PM_{2.5}$ with other pollutant concentrations (CO, NO, NO_2, NO_x, SO_2, O_3) and meteorological parameters (wind speed, relative humidity, solar radiation, atmospheric pressure, air temperature and precipitation) on a daily basis. Principal Component Analysis (PCA) was then employed to identify major air pollution sources at the selected monitoring locations (see e.g. Harrison et al., 1997; So and Wang, 2003; Grivas et al., 2008a), as it is well established that PCA has the ability of reducing the original variables of a large dataset to a smaller number of uncorrelated principal components that explain a large fraction of the total variance (Thurston and Spengler, 1985). For the needs of the study, PCA was applied separately for the cold and the warm period of the year at each monitoring site. The selection of the Principle Components (PCs) was based on the Kaiser's criterion and Orthogonal rotation (specifically VARIMAX rotation) was applied on the components, as it maximizes the sum of the variances of squared loadings, allowing for a better interpretation and also has the advantage of keeping the PCs uncorrelated. Finally, least square regression analysis was used among daily PM_{10} and $PM_{2.5}$ (dependant variables) and NO_x ($NO + NO_2$, as ppb) concentrations (independent variable) to approximate the relative contributions of

combustion and non-combustion sources to the observed PM_{10} and $PM_{2.5}$ levels (Harrison et al., 1997; Liu and Harrison, 2011).

3. Results and discussion

3.1. Seasonal variability of PM_{10} and $PM_{2.5}$

According to Table 1, the seasonal mean PM_{10} and $PM_{2.5}$ concentrations observed in API were the highest. The magnitude of API PM levels, especially during the warm period, can be attributed to the fact that the site receives significant impact from particle emissions related to the activities in the nearby passenger port, which intensify considerably during the summer months.

The 24 h PM_{10} limit value of 50 $\mu g\ m^{-3}$ was exceeded more than 35 times in most sites (with the exception LBL and AAP background stations), breaching the EU short-term air quality standard. On the other hand, the annual PM_{10} limit value of 40 $\mu g\ m^{-3}$ was only exceeded at the traffic LMR station in London (43.6 $\mu g\ m^{-3}$) and API (47.7 $\mu g\ m^{-3}$) in Athens. The latter PM_{10} value was 13% lower than the mean 2001–2004 value reported for the same location by Grivas et al. (2008a). Regarding the $PM_{2.5}$ annual target value of 25 $\mu g\ m^{-3}$, this was only breached in API (35.5 $\mu g\ m^{-3}$) suggesting that both PM_{10} and $PM_{2.5}$ form a public health hazard in API. Although the EU has not included a daily limit value in the $PM_{2.5}$ air quality standard, an assessment of the severity of short-term exposure can be achieved by considering the Air Quality Guidelines (AQG) of the World Health Organization (WHO, 2006). Specifically, the AQG of 25 $\mu g\ m^{-3}$ (99th percentile) proposed for 24-h $PM_{2.5}$ was well exceeded in both stations in Athens (72.7 and 49.8 $\mu g\ m^{-3}$ for API and AAP, respectively), Madrid (51.5 and 41.6 $\mu g\ m^{-3}$ for MPR and MCC) and London (39.9 and 30.8 $\mu g\ m^{-3}$ for LMR and LBR).

Not surprisingly, traffic stations in all 3 cities presented significantly higher concentrations during both seasons compared to the urban background stations. However, the seasonal variability pattern of PM_{10} and $PM_{2.5}$ concentrations presented some differences among cities. At both LMR and LBL, no marked PM seasonal variability was observed. This can be attributed to the fact that both sites are placed in central London, receiving significant impact by traffic-related emissions which are generally distributed uniformly around the year. In addition to that, there is the possibility of instrumentation interference in the observed lack of seasonality. Since semi-volatile compounds, like nitrates, participate in the particle phase mainly during cold conditions (Harrison and Yin, 2008), their loss due to TEOM instrumentation issues (volatilization in the pre-heated sampled air stream) during winter sampling potentially masks seasonal differences (Schwab et al., 2006). It should be noted that the same seasonal effect is also possible for the other two cities, however in London it is expected to be intensified due to the lower cold-period temperatures favouring the particle-phase partitioning of semi-volatile particles (hence, more particle mass is lost). Recent results from measurements using FDMS-TEOMs, which are not affected by the above artifact (since they quantify the mass changes due to evaporative losses) highlight seasonal differences in London, especially in background sites (Harrison et al., 2012). Green et al. (2009) have indicated the possibility of correction of concentrations measured with TEOM at various sites in the UK with non-collocated FDMS data, with rather promising results.

In Madrid, higher PM_{10} concentrations (as well as number of exceedances) were observed at MCC during the warm season. This is probably due to the larger relative contribution of natural particles (e.g. re-suspended dust) (Artíñano et al., 2003), favoured by ground heating and thermal convection prevailing in the dry, semi-arid conditions of the area (Artíñano et al., 2003). The long range transport episodes of Saharan dust particles, which appear with relatively increased frequency during the warm period (Salvador et al., 2004, 2007), possibly form an addition factor for the observed background PM_{10} seasonal variability. On the contrary, the warm–cold period PM_{10} difference at the traffic station in Madrid was not significant, in agreement with findings by Artíñano et al. (2004). On the other hand, higher $PM_{2.5}$ concentrations were observed in Madrid during the cold months as a result of the increased contribution of primary combustion related particles, originating from road-traffic and heating (Artíñano et al., 2001), in addition to high atmospheric stability and the subsidence of the mixing height that leads to reduced mixing of air.

In Athens, both PM_{10} and $PM_{2.5}$ concentrations at API were significantly higher (0.99 confidence level) during the warm period. This can be explained by the intense road transport and the commercial and passenger activity in and around the harbour during July and August. This reverses the decreasing emissions effect which the typical summer holiday period exerts on the overall warm period pollution levels in Athens (Chaloulakou et al., 2005). Additionally, air quality in this coastal area is also aggravated during the warm period by the prevalence of weak sea breeze (Kassomenos et al., 1998) which severely limits ventilation and leads to prolonged particle episodes. For the urban background AAP station, concentrations were also higher during the warm months. Since primary combustion related emissions are less intense at locations of this type, this seasonal variation can be attributed to natural sources (Pateraki et al., 2008) and increased formation of secondary particles during the photochemical season (Grivas et al., 2012).

3.2. Relationship between PM and other pollutants

Correlation analysis was carried out among the daily mean concentrations of particulates (PM_{10} and $PM_{2.5}$) and other gaseous pollutants during the warm and the cold season at all three cities (Table 2). In general, particulates correlated reasonably well with NO_x and CO, suggesting the common road-traffic origin of these pollutants.

Specifically, particulates (PM_{10} and $PM_{2.5}$) were positively correlated with CO with the higher coefficients observed at the traffic sites API, LMR and MPR. As expected, these coefficients were substantially higher during the cold season, when the use of private cars was increased and the meteorological conditions favoured the accumulation of pollutants near the ground. The highest Pearson correlation coefficient between PM_{10} and CO was observed in LMR (0.81). This is probably due to the high percentage of gasoline cars in London and also to the small distance of the site from a heavily trafficked road. The effect of increased CO emissions from older black cabs is also a possibility. In Madrid MPR coefficients ranged between 0.71 and 0.66 (for the cold and the warm period respectively). This seasonal correlation pattern was also observed in API, in agreement with previous findings (Chaloulakou et al., 2003). It is noted that CO was not measured in AAP, where its levels are expected to be very low, close to detection limits. Generally, higher correlations among particulates (PM_{10} and $PM_{2.5}$) and CO are observed in London, as a result of the higher relative contribution of traffic-related PM in London compared to the other two cities. In fact, traffic volumes at Marylebone Road (Charron and Harrison, 2005) exceed those observed on adjacent roads to the traffic sites of API and MPR. In addition to that, while the Bloomsbury site is located in Central London, in Madrid the background site is situated at a larger distance from the city-center.

The correlations among particles and NO, NO_2 and NO_x at LMR (where the highest values were calculated in the majority of cases) and API were generally stronger compared to those between PM

Table 2
Pearson correlation coefficients between daily PM_{10}, $PM_{2.5}$ (in brackets) and gaseous pollutant concentrations averaged over cold and warm seasons in the three measuring sites used.

Site	CO		NO_2		NO		NO_x		O_3		SO_2	
	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm
AAP	–	–	0.44 (0.40)	0.54 (0.45)	0.37 (0.24)	0.38 (0.27)	0.44 (0.37)	0.53 (0.43)	−0.04* (0.26)	0.10* (0.26)	0.26 (0.50)	0.46 (0.49)
API	0.66 (0.61)	0.53 (0.59)	0.60 (0.59)	0.73 (0.79)	0.64 (0.57)	0.74 (0.71)	0.69 (0.66)	0.78 (0.75)	−0.25 (−0.25)	−0.28 (−0.33)	0.51 (0.63)	0.53 (0.52)
LBL	0.64 (0.77)	0.59 (0.58)	0.51 (0.52)	0.57 (0.51)	0.56 (0.66)	0.24 (0.23)	0.57 (0.65)	0.39 (0.36)	−0.34 (−0.45)	−0.01* (−0.07)*	0.55 (0.57)	0.57 (0.53)
LMR	0.81 (0.77)	0.81 (0.76)	0.86 (0.74)	0.87 (0.80)	0.88 (0.79)	0.77 (0.70)	0.92 (0.78)	0.81 (0.74)	−0.73 (−0.63)	−0.60 (−0.58)	0.71 (0.70)	0.74 (0.70)
MCC	0.54 (0.69)	0.32 (0.18)	0.67 (0.79)	0.65 (0.55)	0.60 (0.77)	0.60 (0.48)	0.65 (0.81)	0.60 (0.48)	−0.50 (−0.63)	0.06* (0.17*)	0.52 (0.64)	0.70 (0.59)
MPR	0.71 (0.67)	0.66 (0.70)	0.36 (0.27)	0.51 (0.41)	0.64 (0.63)	0.67 (0.72)	0.63 (0.60)	0.70 (0.71)	−0.40 (−0.32)	−0.32 (−0.19)	0.62 (0.43)	0.65 (0.67)

*All correlations are statistically significant at 99% confidence interval unless indicated with *.
No data were available for AAP CO.

and CO, exhibiting the important associations of PM to combustion-related sources additional to gasoline vehicles. Regarding vehicular sources, a significant percentage of heavy duty vehicles and buses is in circulation (4.1–11.2% in the three areas), while in London and Madrid the penetration of diesel cars in the passenger fleet is noteworthy (22–38%, during the study period). PM-NO_x correlations display strong seasonal variability at most sites. Notably lower correlations between particles and NO_x were recorded at the background sites, where NO_x were dominated by NO_2 and the impact of direct road traffic was suppressed.

The correlation between particulates and SO_2 was generally stronger at the traffic stations than the background sites. Especially, correlations were the strongest in London LMR and in Madrid MPR, probably reflecting the heavy load of diesel passenger cars circulating in these areas, whereas it is noted that diesel vehicle circulation was banned in Athens, until recently.

Finally, daily mean O_3 concentrations correlated negatively with PM_{10} and $PM_{2.5}$ in most cases. This negative correlation can be explained by the reaction of O_3 with NO, which is a major sink of ozone. Only at the background AAP site, statistically significant positive correlations between O_3 and $PM_{2.5}$ were calculated for both seasons, indicating the importance of secondary photochemical processes in the formation of fine particles, in the absence of primary anthropogenic sources (Vassilakos et al., 2005), and due to favourable weather conditions for secondary photochemical pollution formation throughout the year. Comparable results have been reported for urban areas with similar climatic characteristics to those of Athens (e.g. McConnell et al., 1999). However, at LBL and MCC $PM_{2.5}$ are anticorrelated to O_3 during the cold season, whereas in the warm period the anticorrelation is either weak (LBL), or even a marginally significant positive correlation appears (MCC). The weak anticorrelation at LBL during the warm season can be attributed to the fact that warm weather induces the formation of secondary fine particles and ozone, however with a frequency not adequate to form a significant correlation between pollutants. It can be said that the regular anticorrelation is abated to insignificance by the appearance of these photochemical formation events. These seasonal characteristics have been documented specifically for the Bloomsbury site by Joseph (2008). At MCC the limited (in comparison to AAP) distance from emission hotspots does not allow sufficient ageing of the plumes (Plaza et al., 1997) even during favourable conditions (photochemical, wind dispersion). As a result ozone levels remain moderate and specific warm period $PM_{2.5}$-O_3 associations are difficult to detect.

3.3. *Relationship between PM_{10} and $PM_{2.5}$ and meteorological parameters*

The PM_{10} and $PM_{2.5}$ concentrations were negatively correlated with wind speed at all sites, especially during the cold season (Table 3). This was more or less expected, as strong winds are known to disperse locally generated air pollution. However, strong winds can also increase PM levels under certain meteorological conditions due to resuspension of soil and road dust (Kukkonen et al., 2005; Kassomenos et al., 2012), especially in warm and dry environments. The above ideas are consistent with the weaker negative correlations observed between PM and wind speed at almost all sites during the warm period, as well as with the positive correlation between $PM_{2.5}$ and wind speed during the warm period in AAP. The latter indicates the importance of wind-induced transport of secondary particles and gaseous precursors. In many cases, the negative correlation with $PM_{2.5}$ was stronger than with PM_{10}, a fact which represents the moderating effect of wind-suspension of coarse particles from road and other surfaces (Charron and Harrison, 2005).

Table 3
Pearson correlation coefficients between daily PM_{10} and $PM_{2.5}$ concentrations and meteorological parameters ($PM_{2.5}$ in brackets).

Site	Wind speed		Temperature		Relative humidity		Precipitation		Atm. Pressure		Radiation	
	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm
AAP	−0.23 (−0.29)	−0.24 (0.17[b])	0.24 (−0.03[a])	0.47[b] (0.55)	−0.01[a] (−0.19[b])	−0.12[a] (−0.22)	−0.20[b] (−0.22[b])	−0.03[a] (−0.04[a])	0.22 (0.36)	−0.31 (−0.24)	0.23 (0.40)	0.09[a] (0.13[a])
API	−0.49 (−0.59)	−0.23[b] (−0.31)	0.08[a] (−0.05[a])	0.52 (0.66)	0.25 (0.23[b])	−0.21[b] (−0.45)	−0.07[a] (−0.05[a])	−0.18[a] (−0.27)	0.18[b] (0.31)	−0.22[b] (−0.13[a])	0.11[a] (0.33)	0.18[a] (0.23[b])
LBL	−0.43 (−0.36)	−0.45[a] (−0.56[b])	0.01 (−0.10)	0.24 (0.34)	0.07[a] (−0.09[a])	0.07[a] (0.25)	−0.18[b] (−0.08[a])	−0.15[b] (−0.11[a])	0.19[b] (0.14[a])	0.36[a] (0.34[a])	−0.18[a] (0.04[a])	−0.13[a] (0.02[a])
LMR	−0.17 (−0.30)	0.09 (−0.07)	0.38 (0.35)	0.40 (0.43)	0.14 (0.26)	0.07 (0.20[a])	0.04 (0.05)	0.08 (0.12)	0.09 (0.16)	−0.17 (−0.12)	0.19[b] (0.08[a])	0.07[a] (−0.06[a])
MCC	−0.42 (−0.47)	−0.34 (−0.31)	0.09 (−0.02)	0.53[a] (0.55[a])	0.01[a] (0.19[a])	−0.53[a] (−0.46[b])	−0.20[a] (−0.13[a])	−0.14 (−0.12[a])	0.33[a] (0.35[a])	0.12 (0.02)	0.02[a] (0.11[a])	0.07[a] (0.06[a])
MPR	−0.34 (−0.38)	0.03[a] (−0.27)	0.31 (0.18)	0.56 (0.45)	0.03[a] (0.03[a])	−0.44 (−0.38)	−0.23 (−0.20)	−0.10 (−0.06)	0.33 (0.27)	0.03 (0.22)	0.03 (0.08)	−0.09 (0.09)

All correlations are statistically significant at 99% confidence interval (unless otherwise indicated).
[a] Correlation not significant.
[b] Correlation significant at 95% confidence level.

The correlation between temperature and PM was positive during warm season probably due to the increased contribution of secondary particles. Specifically, in the southern European cities of Madrid and Athens, correlations were found in the range of 0.45–0.66 both for PM_{10} and $PM_{2.5}$ at all sites during the warm season, in accordance with the previously identified enhanced production of sulphate and organic carbon particles during the summer months (Theodosi et al., 2011; Grivas et al., 2012). The slightly higher correlation for $PM_{2.5}$ than for PM_{10} also supports the above hypothesis, since the majority of OC and especially sulphate ions are found in the fine fraction (Artíñano et al., 2003; Harrison et al., 2004; Theodosi et al., 2011).

AAP, API, MCC and MPR also presented significant negative correlations between PM and relative humidity during the warm season, suggesting a larger impact of re-suspended dust associated with dry conditions during warm months.

Additionally, negative correlations between PM concentrations and daily amount of precipitation were observed at almost all sites during both seasons. However, these correlations were not statistically significant in most cases in Madrid and Athens, probably due to the limited amounts of rainfall in these regions especially in summertime. Furthermore, positive correlations between particles and atmospheric pressure at all sites during the cold season confirmed the hypothesis of reduced pollutant dispersion associated with stable atmospheric conditions. Finally, the correlations between solar radiation and particle concentrations were not statistically significant.

3.4. Principal Component Analysis

In the next phase, PCA was applied to identify uncorrelated factors explaining the observed variance in the air quality datasets. As a principle, the Kaiser criterion was used and in most cases 4 PCs were obtained, accounting for more than 90% of the dataset variance (Table 4). The inclusion of a fourth possible component was checked in Athens. However, no specific physical or source-related process could be associated with the fourth PC and thus only 3 components were retained. For the purposes of the following discussion, loadings with absolute values larger than 0.5, in the range of 0.2–0.5 and lower than 0.2 are characterized as high, moderate and weak, respectively (weak loadings are suppressed in Table 4).

Specifically in API, the road traffic factor (PC1) accounted for a large percentage (56–64%) of the total variance during both seasons, indicating traffic emissions as the main air pollution source in the area. PC2 displayed generally high NO_2 and SO_2 loadings (>0.5) accompanied by PM loadings in the range of 0.32–0.43, revealing the moderate association between PM and fuel oil combustion point emissions from vessels inside the port area and activities in the industrial areas in the vicinity (NW and NE) of the site. PC3 is indicative of the road level ozone titration reaction, explaining, however, only a small portion of the dataset variance (9–12%).

On the other hand, in AAP, PM fractions were classified in a separate PC than primary traffic-related gaseous pollutants. The PM related factor accounted for 29–48% of the variance observed during the two seasons, highlighting the increased importance of particle formation processes (secondary and natural) additional to road traffic. PC2 explained 25–30% of the variance and accounted for road level emissions, characterized by very high loadings (>0.8) in NO_x and negative associations with O_3. PC3 (13–22% of variance explained) was heavily associated to O_3, indicating photochemical activity, which also seems to influence fine particles (a high loading was also registered for NO_2 in the warm period, signifying it's increased secondary production in the background location). Finally, PC4, since area-background SO_2 concentrations are considered for this station, appears to be associated with regional

Table 4
Principal component loadings and variance explanation for air quality data obtained in the three cities (component loadings lower than 0.20 are suppressed).

	Cold season				Warm season			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
AAP								
NO	–	**0.92**	−0.23	–	–	**0.94**	–	−0.25
NO_2	0.36	**0.78**	–	0.37	0.32	**0.59**	**0.57**	–
O_3	–	−0.21	**0.92**	0.25	0.20	−0.31	**0.95**	–
SO_2	–	–	0.27	**0.93**	0.20	–	–	**0.92**
PM_{10}	**0.98**	–	–	–	**0.96**	–	–	–
$PM_{2.5}$	**0.77**	–	**0.55**	0.22	**0.94**	–	0.29	0.31
Variance (%)	28.8	25.4	21.5	18.8	47.6	29.8	12.9	5.1

	Cold season			Warm season		
	PC1	PC2	PC3	PC1	PC2	PC3
API						
CO	**0.88**	–	–	**0.67**	–	**0.59**
NO	**0.56**	0.34	**0.70**	**0.61**	**0.51**	0.46
NO_2	0.37	**0.81**	–	**0.66**	**0.53**	0.39
O_3	–	–	**−0.98**	–	–	**−0.94**
SO_2	–	**0.93**	–	0.26	**0.93**	–
PM_{10}	**0.85**	0.43	–	**0.81**	0.36	–
$PM_{2.5}$	**0.82**	0.41	–	**0.91**	0.32	–
Variance (%)	55.7	19.4	12.4	64.2	14.9	9.3

	Cold season				Warm season			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
LBL								
CO	**0.75**	0.42	0.33	0.31	–	0.48	**0.50**	**0.58**
NO	**0.78**	0.30	0.38	0.35	**0.88**	–	0.38	–
NO_2	0.33	0.23	**0.57**	**0.61**	**0.78**	0.35	–	0.40
O_3	−0.30	–	**−0.90**	−0.22	−0.39	–	**−0.87**	–
SO_2	0.30	0.30	–	**0.85**	0.25	0.30	–	**0.89**
PM_{10}	–	**0.93**	0.22	0.24	–	**0.93**	–	0.29
$PM_{2.5}$	0.36	**0.88**	–	–	–	**0.96**	–	0.20
Variance (%)	23.1	29.6	21.2	20.6	23.7	31.6	17.1	20.2
LMR								
CO	**0.76**	0.41	0.36	0.22	**0.79**	0.40	0.32	0.22
NO	**0.79**	0.41	0.29	0.35	**0.83**	0.30	0.36	0.23
NO_2	**0.76**	0.35	0.33	0.38	**0.75**	0.43	0.27	0.38
O_3	0.36	−0.27	**−0.86**	−0.25	−0.39	−0.23	**−0.88**	–
SO_2	0.36	0.33	0.27	**0.83**	0.29	0.35	–	**0.87**
PM_{10}	**0.51**	**0.71**	0.26	0.33	0.48	**0.77**	–	0.35
$PM_{2.5}$	0.35	**0.85**	0.25	0.27	0.33	**0.86**	0.25	0.28
Variance (%)	34.3	26.7	18.0	17.7	34.9	27.7	17.2	17.7
MCC								
CO	**0.84**	0.29	0.25	0.33	**0.98**	–	–	–
NO	**0.70**	0.37	**0.51**	0.20	0.23	0.21	0.64	**0.66**
NO_2	0.49	0.44	**0.57**	0.39	0.25	0.47	**0.53**	**0.60**
O_3	−0.30	−0.24	**−0.86**	−0.30	−0.06	–	**−0.96**	–
SO_2	0.39	0.26	0.41	**0.77**	–	0.43	0.28	**0.85**
PM_{10}	–	**0.94**	–	–	–	**0.90**	–	0.32
$PM_{2.5}$	0.38	**0.84**	0.30	–	–	**0.96**	–	0.21
Variance (%)	26.4	30.7	24.0	15.0	16.0	31.8	23.5	24.3
MPR								
CO	**0.61**	0.26	0.38	**0.60**	**0.83**	0.32	0.28	0.22
NO	**0.61**	–	0.49	**0.54**	**0.83**	0.33	0.31	0.22
NO_2	–	–	0.23	**0.92**	0.27	0.20	–	**0.93**
O_3	–	–	**−0.93**	−0.28	−0.26	–	**−0.95**	–
SO_2	0.25	0.33	0.22	**0.85**	**0.86**	0.27	0.20	0.27
PM_{10}	0.47	**0.82**	–	0.25	0.30	**0.84**	0.21	0.30
$PM_{2.5}$	**0.89**	0.35	–	–	**0.61**	**0.69**	–	–
Variance (%)	26.3	14.5	19.8	33.9	39.1	21.8	16.7	16.2

transport processes of pollution (most probably generated by stationary sources, related to industrial activity and domestic heating), also involving fine particles (Markakis et al., 2010).

In LBL, PC1 explained 23–24% of the total variance and indicated road level sources, since it contained the primary gaseous pollutant variables, while PM were segregated at the second component (PC2 accounting for 30–32% of the variance). The ozone dynamics at background London (as captured by the PCA analysis at PC3), appear to contrast those prevailing at background Athens, most probably due to the absence of the complex climatologic-topographic regime responsible for ozone transport and formation in the latter. Combustion emissions from point sources were accountable for the observed profile in the final component (PC4, explaining 20–21% of dataset variance).

In LMR, the road traffic component (PC1) explained, as expected, a larger part of the variance (34–35%) than at LBL, but in this case

Table 5
Linear least square regression coefficients for the relationships $[PM_{10}] = R_1 \times [NO_x] + C_1$ and $[PM_{2.5}] = R_2 \times [NO_x] + C_2$ ($PM_{2.5}$ calculations in brackets).

Site	Slope cold	Slope warm	Intercept cold	Intercept warm	R cold	R warm
AAP	0.46 ± 0.08 (0.22 ± 0.06)	0.71 ± 0.09 (0.37 ± 0.06)	11.00 ± 2.26 (8.96 ± 1.57)	16.31 ± 2.21 (14.04 ± 1.56)	0.46 (0.37)	0.53 (0.43)
API	0.24 ± 0.03 (0.18 ± 0.03)	0.33 ± 0.03 (0.25 ± 0.02)	11.43 ± 4.55 (6.93 ± 3.65)	10.99 ± 3.41 (7.37 ± 2.42)	0.69 (0.64)	0.75 (0.78)
LBL	0.08 ± 0.01 (0.06 ± 0.01)	0.11 ± 0.00 (0.06 ± 0.01)	16.44 ± 1.24 (5.54 ± 0.73)	17.82 ± 1.74 (7.81 ± 1.04)	0.57 (0.65)	0.39 (0.36)
LMR	0.09 ± 0.00 (0.04 ± 0.00)	0.08 ± 0.00 (0.04 ± 0.00)	16.36 ± 1.23 (7.64 ± 0.79)	21.58 ± 1.36 (9.04 ± 0.79)	0.88 (0.78)	0.81 (0.74)
MCC	0.50 ± 0.04 (0.27 ± 0.02)	0.76 ± 0.08 (0.70 ± 0.03)	10.82 ± 1.97 (4.66 ± 0.65)	20.02 ± 1.74 (9.16 ± 0.23)	0.65 (0.81)	0.59 (0.48)
MPR	0.18 ± 0.02 (0.09 ± 0.01)	0.23 ± 0.02 (0.06 ± 0.01)	11.66 ± 2.84 (7.98 ± 0.58)	14.85 ± 1.99 (9.86 ± 0.66)	0.63 (0.75)	0.69 (0.44)

The intercept represents the mean non-combustion component.

also presented moderate, yet significant, loadings in PM (0.3–0.5). However, a second component was extracted, heavily relying on PM (PC2 explaining 27–28% of the total variance) and denoting correlation patterns of particle concentrations significantly deviating from those observed in typical heavy traffic conditions. The remaining two components were similar to the respective components extracted from the LBL dataset.

A traffic component (PC1) explaining 16–26% of the total variance was identified in MCC. This factor was associated with high CO and NO loadings accompanied by moderate $PM_{2.5}$ and SO_2 loadings during the cold season, while during the warm season PC1 was associated with a high CO loading accompanied by moderate NO and NO_2 loadings, suggesting road traffic as the related source for both seasons. Particle variables, at this background site, were classified separately from road-level primary gaseous pollutants, in a component explaining 31–32% of the total variance and suggesting the possible impact of non-anthropogenic emissions and regionally evolving secondary processes. The third component accounted for 24% of the total variance and was associated to strongly negative O_3 loadings and reasonably high NO and NO_2 loadings, characteristic of the reactivity in the NO_x–O_3 system. PC4 explained 15–24% of the total variance and presented high SO_2 loadings indicating stationary fuel combustion as the main related source. High loadings in NO_x, exclusive to the warm season, could be tentatively attributed to some regional secondary transport process, affecting the background site.

Finally, at the traffic MPR site, the traffic-related component explained 26–39% of the total variance. In contrast to the background site, fine particles were included in this factor as well, signifying the importance of road-level particle emissions. PM_{10} was highly associated with a separate component (accounting for 15–22% of the variance) possibly reflecting the fact that in the study area of Madrid, non-traffic sources like wind-induced resuspension, LRT, and for the warm period secondary-regional processes (represented by the high $PM_{2.5}$ correlation) significantly affect particle levels. The ozone-specific component (PC3, explaining 17–20% of the total variance) reappears at the traffic station, being again largely unrelated to particle indicators. The fourth component at this site (PC4, capturing 16–34% of the total variance), is characteristic of stationary combustion but specifically gauged towards space heating emissions, given the absence of a high SO_2 loading during the warm period (while at the same time, the traffic components include SO_2 only during the warm period).

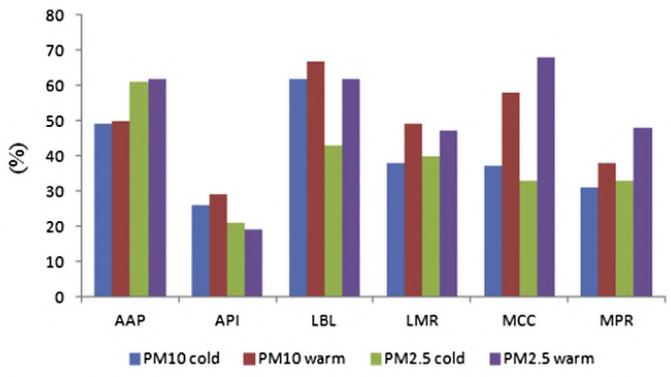

Fig. 1. Non-combustion related PM fraction (expressed in % of total PM) in Athens, Madrid and London.

3.5. *Non-combustion related PM_{10} and $PM_{2.5}$*

In the next step, Linear Regression Analysis was applied to estimate the non-combustion related PM in the three cities. Daily mean PM_{10} and $PM_{2.5}$ concentrations were therefore regressed against NO_x separately for the warm and the cold period of the year (Table 5). The intercepts of the derived least squares regression equations were assumed to represent the non-combustion fraction of PM_{10} and $PM_{2.5}$ in the three cities (Harrison et al., 1997).

In Table 5 a significant variation in slopes is observed for the different traffic sites reflecting the different traffic characteristics. The examination of PM/NO_x emission ratios for various vehicle categories (UK data from the NAEI) revealed that the lowest slope observed at LMR is probably due to larger number of HDDV and buses in the London fleet during the study period, as compared to the other two cities. Also, the large penetration of diesel cars in the fleet of Madrid, as compared to Athens, where it was practically zero, leads to lower PM/NO_x ratios in MPR than in API.

The linear regression analysis results as presented in Fig. 1 varied substantially among sites and seasons. Specifically, the non-combustion PM_{10} contribution at MCC was found 37–58%, while at MPR it was 31–38% depending on the season. The respective contributions to $PM_{2.5}$ were 33–68% at MCC and 33–48% at MPR. The above findings for the traffic station in Madrid are in agreement with the source apportionment analysis conducted by Querol et al. (2004a) who allocated 34% of PM_{10} to non-combustion related sources. Comparable results were also reported from a mass closure analysis (Artíñano et al., 2003), where combustion unrelated sources (crustal and marine) were found to sum up to 22–44% of the reconstructed $PM_{2.5}$ and PM_{10} mass, respectively. Higher non-combustion contributions to PM_{10} for urban background sites in Madrid, in comparison to traffic orientated sites, were also confirmed by Salvador et al. (2011).

In London LBL the non-combustion contribution to the total PM_{10} ranged between 62 and 67% in LBL and 38 and 49% in LMR. Regarding $PM_{2.5}$, the non-combustion contribution ranged between 43 and 62% at LBL and 40 and 47% at LMR. These findings are in agreement with Stedman et al. (2001) who applied receptor modelling for PM_{10} concentrations in LBL, using a regression methodology similar to the present one, and reported comparable results for primary non-combustion particles. The traffic-background differences for the non-combustion contributions were also reported by the mass closure study of Harrison et al. (2004), at multiple roadside-urban background site pairs in London.

In Athens, the non-combustion-related component accounted for 26–29% of the PM_{10} measured at API, in accordance with past estimates for a kerbside monitoring location in downtown Athens (Chaloulakou et al., 2005), while at the background site the non-combustion related component was significantly higher and reached 49–50%. Regarding $PM_{2.5}$, the non-combustion fraction ranged around 20% in API and 60% in AAP. These findings are in agreement with a receptor modelling analysis conducted by Grivas et al. (2008b), which attributed less than 30% of $PM_{2.5}$ to sources unrelated to fuel combustion at a traffic location in Athens. Additionally, the PMF source apportionment study of Karanasiou et al. (2009) conducted at residential locations in the periphery of the Athens basin reported high combustion unrelated PM levels, relevant to those presently estimated at AAP.

On the whole, it is apparent that the non-combustion fraction was generally higher during the warm season, probably because of resuspension due to dry and hot conditions. Moreover, in Athens, prevailing sea breeze circulations during the summer months (Kassomenos et al., 1995), can potentially transport marine aerosols deep in the basin (Pateraki et al., 2008). Not surprisingly, the highest non-combustion PM contributions were observed in the background stations, whereas in the traffic sites the seasonal variance was also weaker (Fig. 1), reflecting the steady dominance of the combustion-related fractions throughout the year. It is worth mentioning that the highest PM_{10} non-combustion fraction was observed in LBL, while the highest $PM_{2.5}$ non-combustion fraction was found in AAP, which, among the three background sites examined, is the most secluded from urban emissions.

4. Conclusions

In this study we explored the possibility of using only publicly available, fixed-site, pollutant and meteorological data in order to characterize the spatial and seasonal variability of PM levels and to identify their main sources. The study provided a practical methodology for analysing multi-site air quality and meteorological time-series, in order to gain insight into the factors affecting PM_{10} and $PM_{2.5}$ levels in urban areas. The analysis focused on three European capital cities (Athens, London and Madrid) and investigated the sources and factors affecting PM_{10} and $PM_{2.5}$ levels at traffic/background monitoring sites.

All three traffic sites (as well as the Madrid background site) breached the EU legislated 24 h PM_{10} limit value, while the annual PM_{10} limit value of 40 $\mu g\ m^{-3}$ was exceeded at the traffic stations of London and Athens but not in Madrid. On the other hand, the EU annual $PM_{2.5}$ target value was only breached in the traffic station of Athens, which also reported the highest PM_{10} and $PM_{2.5}$ seasonal means, suggesting that both coarse and fine particles form a public health hazard in the area. Nevertheless, these values were markedly lower, than those reported for Athens in previous years (Grivas et al., 2008a).

The seasonal variability pattern of particulates presented differences among different cities and sites. Although in London no marked seasonal variability was observed, higher PM_{10} concentrations were observed in Athens and Madrid during the warm period, suggesting the larger relative contribution of secondary and natural particles during hot and dry days and establishing an important geographical contrast between North and Southern Europe. On the other hand, higher $PM_{2.5}$ concentrations were observed in Madrid during the cold season (roughly 3%, according to local traffic data), due to the increased loads of traffic, the higher atmospheric stability and the subsequent reduced mixing height. Nevertheless, a part of the inter-urban contrasts may be attributed to the different monitoring techniques used in the three cities.

Significant positive correlations were found between particulates and CO, with the higher values reported at the traffic station of London, probably due to very high traffic volumes at the adjacent road. On the other hand, the weaker correlations in Athens can be attributed to the existence of more wind-blown dust, sea-salt and secondary particles in the area. Stronger correlations between particles and SO_2 at the traffic stations, rather than the background sites, indicated the important contribution from road-level emissions for both pollutants. Finally, negative correlations among particulates and O_3 indicated ozone titration under the influence of primary traffic emissions, whereas the positive correlation between $PM_{2.5}$ and O_3 observed in the Athens background site suggested the importance of secondary photochemical processes in the formation of secondary particles, especially in the absence of primary anthropogenic sources.

PCA results varied substantially between and within study areas, reflecting the different traffic intensity and patterns, as well as the different climatic conditions. The derived factors were associated with traffic conditions, non-traffic particle sources, photochemical activity and fuel combustion from stationary sources. Not surprisingly, the traffic-associated factor accounted for larger fractions of the total variance at the traffic stations, while the ozone-related factor had higher loadings in the south European cities of Athens and Madrid.

The estimated non-combustion fraction of PM varied substantially among cities, sites and seasons. Specifically, the non-combustion related PM was generally higher during the warm season, one probable cause being resuspension due to dry and hot conditions. As expected, the highest non-combustion PM contributions were observed in the background stations, whereas in the traffic sites the seasonal variance was also weaker, reflecting the steady dominance of the combustion-related fractions throughout the year in these areas.

On the whole, the analysis provided evidence of the substantial impact of non-combustion sources (e.g. road-dust resuspension) on local air quality in all three cities. Thus, it became clear that measures designed to reduce vehicular exhaust emissions may have a rather limited effect on urban background PM and, therefore, additional measures may also be needed in these areas. For instance, the effectiveness of measures addressing soil and road-dust resuspension, such as street sweeping/washing, should also be examined in these urban settings. Nevertheless, the above do not cancel out the need for reducing the combustion-related aerosols through traffic mitigation strategies and urban planning, as these could also reduce part of the non-combustion traffic emissions, as well as the concentrations of the more toxic compounds.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.01.004.

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